

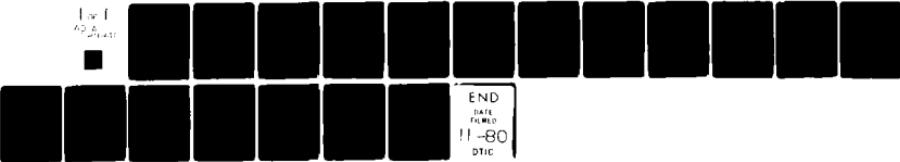
AD-A089 940

NORTH CAROLINA UNIV AT CHAPEL HILL DEPT OF CHEMISTRY F/G 7/3
SYNTHESIS AND CHARACTERIZATION OF METALLO-ORGANIC CONDUCTING MA-ETC(U)
SEP 80 W E HATFIELD N00014-76-C-0816
NL

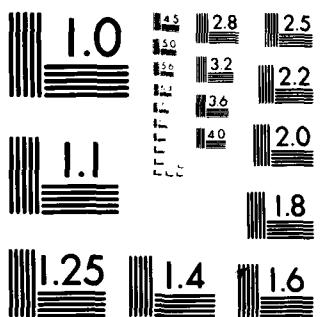
UNCLASSIFIED

TR-12

1 of 1
AD-A089 940



END
DATE FILMED
11-80
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS

AD A089940

LEVEL
AUG 3 1980
12

OFFICE OF NAVAL RESEARCH

Contract No 0014-76-C-0816
Task No. NR 053-617
TECHNICAL REPORT NO. 12

Synthesis and Characterization of Metallo-organic
Conducting Materials with Tetraazaannulenes

by

William E. Hatfield

Prepared for Publication

in

Symposium Series: Conductive Polymers
Plenum Press



University of North Carolina
Department of Chemistry 045A
Chapel Hill, North Carolina 27514

1115 September 5, 1980

Reproduction in whole or part is permitted for any purpose of
the United States Government.

*This document has been approved for public release and sale;
its distribution is unlimited.

*This statement should also appear in Item 10 of Document Control Data
- DD Form 1473. Copies of form available from cognizant contract
administrator.

DDC FILE COPY

400342

80 10 1 055

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 12	2. GOVT ACCESSION NO. AD-A089 940	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Synthesis and Characterization of Metallo-organic Conducting Materials with Tetraazaannulanes		5. TYPE OF REPORT & PERIOD COVERED Technical Report	
7. AUTHOR(s) William E. Hatfield		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0816	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of North Carolina Chapel Hill, NC 27514		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE September 5, 1980	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 13	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited			
17. DISTRIBUTION STATEMENT (at the abstract entered in Block 20, if different from Report) This document has been approved for public release and sale; its distribution is unlimited.			
18. SUPPLEMENTARY NOTES To be published in Plenum Press Symposium Series: "Conductive Polymers"			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Mixed-valence, electrical conductivity, crystal structure, macrocyclic complexes, nonstoichiometric compounds. <i>mixed valence metal complexes</i> <i>Cu⁽⁺²⁾ Ni⁽⁺²⁾ Pd⁽⁺²⁾ Pt⁽⁺²⁾</i>			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Compounds of macrocyclic ligand [4,11-dihydro- <i>o</i> -benzo[<i>b,i</i>][1,4,8,11]tetraaza-[14]annulene, dB-TAA, have been prepared with Cu ²⁺ , Ni ²⁺ , Pd ²⁺ , Pt ²⁺ . The palladium complex crystallizes in three crystalline modifications, two of which are similar to the structurally characterized compound Ni(dB-TAA), while the third form packs as cofacial dimers in the solid state. Partial oxidation of Pd(dB-TAA) ($\sigma = 0.4 \text{ ohm}^{-1} \text{cm}^{-1}$, $\Delta E = 0.04-0.06 \text{ eV}$), Pt(dB-TAA)I _{1.35} ($\sigma = 0.12 \text{ ohm}^{-1} \text{cm}^{-1}$, $\Delta E = 0.06-0.12 \text{ eV}$), and Pt(dB-TAA)I _{1.50} ($\sigma = 0.03 \text{ ohm}^{-1} \text{cm}^{-1}$).			

Accession For	<input checked="" type="checkbox"/>	<input type="checkbox"/>
NTIS Gr. & I	<input type="checkbox"/>	
DTIC T-B	<input type="checkbox"/>	
Unannounced	<input type="checkbox"/>	
Justification	<input type="checkbox"/>	
BY	<input type="checkbox"/>	
Distribution/ Availability Classes	<input type="checkbox"/>	
Avail. to Foreign Countries	<input type="checkbox"/>	
Printed or Special	<input type="checkbox"/>	

A

SYNTHESIS AND CHARACTERIZATION OF METALLO-ORGANIC CONDUCTING MATERIALS WITH TETRAAZANNULENES

William E. Hatfield

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

INTRODUCTION

Intensive research activities in university, industrial and national research laboratories on mixed valence organic and metallo-organic compounds have led to insights into the chemical and structural features which determine such physical properties as magnetic behavior and electrical conductivities.¹ The aim of the research is the production of new materials with properties which may be exploited in technological applications, with the expected dividends being the discovery of new phenomena, the invention of new experimental methods, and the development of new theoretical models. The recent observation² of superconductivity in bis(tetramethyltetraselenafulvalene)hexafluorophosphate, $(\text{TMTSF})_2\text{PF}_6$, provides an excellent example of the successes which may be expected as this research area is expanded and developed.

An X-ray structural study³ has shown that the nickel complex of the ligand (4,11-dihydro-dibenzo[b,i][1,4,8,11]tetraaza[14]annulene Ni(dB-TAA), is essentially planar, and that the molecules pack in slipped stacks in the solid state. Even though the slipped nature of the stacks results in a long nickel-nickel distance in adjacent molecules of 5.228 Å, the interplanar separations between crystallographically inequivalent molecules are 3.235 and 3.295 Å. These distances are slightly shorter than the 3.35 Å interplanar separation in graphite and permit extensive π-π interactions between adjacent molecules, thus making partially oxidized analogues good candidates for systematic studies of structural and chemical effects on electrical conductivities.

This paper presents a brief survey of research on mixed valence tetraazaannulene complexes which is underway in our laboratory. As noted in the reference citations much of this work is being carried out in collaboration with research groups at the University of North Carolina and at Texas A & M University.⁴ Systems to be discussed in this Symposium Article include a series of macrocyclic tetraazaannulene complexes with Cu²⁺, Ni²⁺, Co²⁺, Pd²⁺, and Pt²⁺ and their partially oxidized reaction products. These complexes will be designated as M(dB-TAA) in the following sections. As will be shown the electrical conductivities and activation energies of some of these compounds approach those of the partially oxidized metallo-phthalocyanines which exhibit metal-like temperature dependencies of σ , and of the partially oxidized metalloporphyrins.⁵

EXPERIMENTAL SECTION

Synthetic Procedures. - Complexes of copper(II), nickel(II), cobalt(II), palladium(II), and platinum(II) with the tetraazaannulene were prepared⁶ in good yield by an initial reaction of a metal salt (the acetate in the case of copper(II), nickel(II), and cobalt(II); K₂PdCl₄; or K₂PtCl₄) with o-phenylenediamine in ethylene glycol, followed by addition of Na⁺C₃H₃O₂⁻. The reaction mixtures thus obtained were stirred at reflux for 5 hours, cooled to room temperature, and the products collected by filtration. The crude products were washed with ethanol, acetone, and diethyl ether, and air dried. Highly purified samples were obtained by vacuum sublimation (350°C; 0.005 mm Hg). Analytical data for carbon, hydrogen, and nitrogen on the metallocycles differed from the calculated values by less than 0.03% in all cases.

Oxidation with Iodine. - After refluxing for 16 hours in chlorobenzene in the presence of an initial ten-fold excess of iodine, Pd(dB-TAA) yields Pd(dB-TAA)I_{2.0}. The mixed valence compounds Pt(dB-TAA)_{1.35} and Pt(dB-TAA)_{1.5} result from heating Pt(dB-TAA) in 1,2,4-trichlorobenzene at 200°C in the presence of a ten-fold excess of iodine for 16 and 24 hours, respectively. The resonance Raman spectra of these materials using 488 nm excitation exhibited bands at 105-115 cm⁻¹ with overtones near 210 cm⁻¹, values which are consistent with the presence of polyiodide counterions. Attempts to obtain single crystals for structural and conductivity studies are underway.

Electrical Conductivities. - Electrical conductivities of pressed pellet samples were determined by a four probe d.c. method using the van der Pauw technique. The pellets, which were 1.3 cm in diameter and approximately 0.2 cm thick, were compacted using a Beckman KBr die and a ring press operated routinely at ten tons

of pressure. A Keithley Model 227 constant current source, which was operated typically at 10 μ amp, and a Keithley Model 180 nanovoltmeter were used to measure the electrical conduction properties. Electrical contacts were made with silver paste. Pellets which did not provide ohmic characteristics were rejected. Activation energies were determined from temperature variation studies of the electrical conductivities in the range 77 to 300 K using a glass Dewar equipped with a sample holder which was fitted with resistance heater and temperature sensors. Temperatures were measured with a calibrated platinum resistance thermometer. Measurements were made in an isothermal mode provided by the resistance heater, radiation heat leak to the cryogen, and a Lake Shore Cryotronics Model DTC-500 temperature controller. Room temperature conductivities and activation energies, where available, are summarized in Table I where it may be seen that partial oxidation of the macrocyclic complexes leads to a great enhancement of the electrical conductivities of the materials.

Table I. Electrical Conductivities and Activation Energies for
 $M(dB-TAA)I_x$

Compound	σ , $\text{ohm}^{-1}\text{cm}^{-1}$ (R.T.)	ΔE , eV
Cu(dB-TAA)	$<10^{-8}$	
Ni(dB-TAA)	$<10^{-8}$	
Co(dB-TAA)	$<10^{-8}$	
Pb(dB-TAA)	$\sim 10^{-9}$	
Pt(dB-TAA)	$\sim 10^{-8}$	
Pd(dB-TAA) $I_{2.01}$	0.4	0.04-0.06
Pt(dB-TAA) $I_{1.35}$	0.12	0.06-0.12
Pt(dB-TAA) $I_{1.50}$	0.03	

Magnetic Susceptibility Measurements. - Magnetic susceptibility data were collected using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM). The vibrating sample magnetometer was operated from zero-field to 10 kOe. The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365) and associated field control unit (Magnion FFC-4 with a Rawson-Lush model 920 MCM rotating-coil gauss meter) were calibrated against NMR resonances (^{1}H and ^{3}Li) over the field range 0.35 - 10 KOe and found to be linear to within better than 1% over the entire range. The field set accuracy is within $\pm 0.3\%$ at 300 gauss and better than 0.15% at 10,000 gauss. The magnetometer was calibrated with HgCo(NCS)_4 .⁷ Powdered samples of the calibrant and compounds used in this study

were contained in precision milled Lucite sample holders. Approximately 150 mg. of each were used. Diamagnetic corrections for the constituent atoms were estimated from Pascal's constants.⁸⁻¹⁰

Other Physical Measurements. - Electron paramagnetic resonance spectra were obtained by use of a Varian E-3 spectrometer. Infrared spectra of samples contained in KBr pellets were recorded on a Beckman IR 4250 spectrophotometer. Electronic spectra in the UV-visible range were obtained with a Cary 17I spectrophotometer on solutions of the compounds in CHCl₃ or Nujol mulls mounted between quartz plates. Resonance Raman spectra were taken on micro-crystalline samples with 448 nm excitation. Elemental analyses were carried out by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

X-Ray Diffraction Data Collection. - Diffraction data were collected on an Enraf-Nonius CAD4 automatic diffractometer with molybdenum radiation and a graphite monochromator. Accurate cell dimensions were obtained by least squares refinement of the diffractometer angle settings for 25 reflections. Procedures for the collection of intensities, calculation of scan widths, and background measurements have been described in detail elsewhere.¹¹ There were 3472 unique reflections for the monoclinic crystal [β -Pd(dB-TAA)] described below, of which 2361 had $F_o^2 > 3\sigma(F_o^2)$. There were 1658 unique reflections for the orthorhombic crystal [γ -Pd(dB-TAA)] of which 1001 had $F_o^2 > 1\sigma(F_o^2)$. Three dimensional Patterson analyses were used to locate the metal atoms, and the other non-hydrogen atoms were located from different Fourier maps. After further refinement of the atomic positions most of the hydrogen atoms were located from subsequent Fourier maps, with the remaining hydrogen positions being calculated. Absorption corrections were made on the data for both crystals and refinement at convergence yielded final values of $R = 0.042$ and $R^W = 0.048$ for the monoclinic crystal and $R = 0.044$ and $R^W = 0.033$ for the orthorhombic crystal. Full matrix least squares refinement was based on F , and the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and $w = [2F_c/\sigma(F)]^2$.

RESULTS

X-ray crystallographic studies have revealed that there are at least three crystalline forms of Pd(dB-TAA).¹¹ One of these, designated α -Pd(dB-TAA), which was obtained by vacuum sublimation of the crude reaction product crystallizes in the monoclinic system with $a = 19.426(23)$, $b = 5.292(7)$, $c = 14.838(3)$, and $\beta = 112.32(8)$. Based on the similarity in the structural data for α -Pd(dB-TAA) and Ni(dB-TAA) which is summarized in Table II, it is reasonable to conclude that the two compounds are isostructural, with planar α -Pd(dB-TAA) molecules stacking in a slipped fashion.

A second crystalline form of the palladium compound, β -Pd(dB-TAA), was obtained from the batch of crystals which yielded α -Pd(dB-TAA). The structure

Table II Unit Cell Data for Ni(dB-TAA) and α -Pd(dB-TAA)

Compound	a, Å	b, Å	c, Å	β , deg
Ni(dB-TAA) ^a	19.456(4)	5.228(1)	14.868(3)	112.28(1)
α -Pd(dB-TAA) ^b	19.426(23)	5.292(7)	14.838(3)	112.32(8)

^aReference 4.

^bReference 11.

of Pd(dB-TAA) has now been solved by X-ray crystallography. A view of a single molecular unit is given in Figure 1, and some important molecular dimensions are given in Table III. The material crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 8.974(8)$, $b = 10.985(10)$, $c = 14.617(10)$, and $\beta = 95.14(9)$. Although all atoms sit on general positions, the molecule is very nearly planar, with the largest deviation from the best least squares plane for all non-hydrogen atoms being $0.047(.010)\text{\AA}$ for an apical carbon (C11) of one of the propane-1,2-diiminato exocyclic rings. The palladium atom lies at $-0.035(.001)\text{\AA}$ with respect to this plane. In a similar calculation, the palladium atom sits at $-0.016(.001)\text{\AA}$ from the best least squares plane formed by the four nitrogen donor atoms.

As shown in Figure 2, the packing of the molecules in the solid state is distinctly different from that exhibited by the nickel analogue. Instead of the slipped molecular stacking as occurs in Ni(dB-TAA), the molecules of β -Pd(dB-TAA) are arranged in pairs. The shortest palladium-palladium distance is $4.382(1)\text{\AA}$, with the next shortest distance between palladium atoms in adjacent pairs being 6.643\AA . The closest contact of the palladium ion with an adjacent molecule of a given pair is to C9 with Pd-C9' being $3.432-(4)\text{\AA}$. Other close contacts are Pd-N2' of $4.178(4)\text{\AA}$ and Pd-N3' of $3.645(4)\text{\AA}$. The Pd-C9'-Pd' angle is $88.02(11)^\circ$.

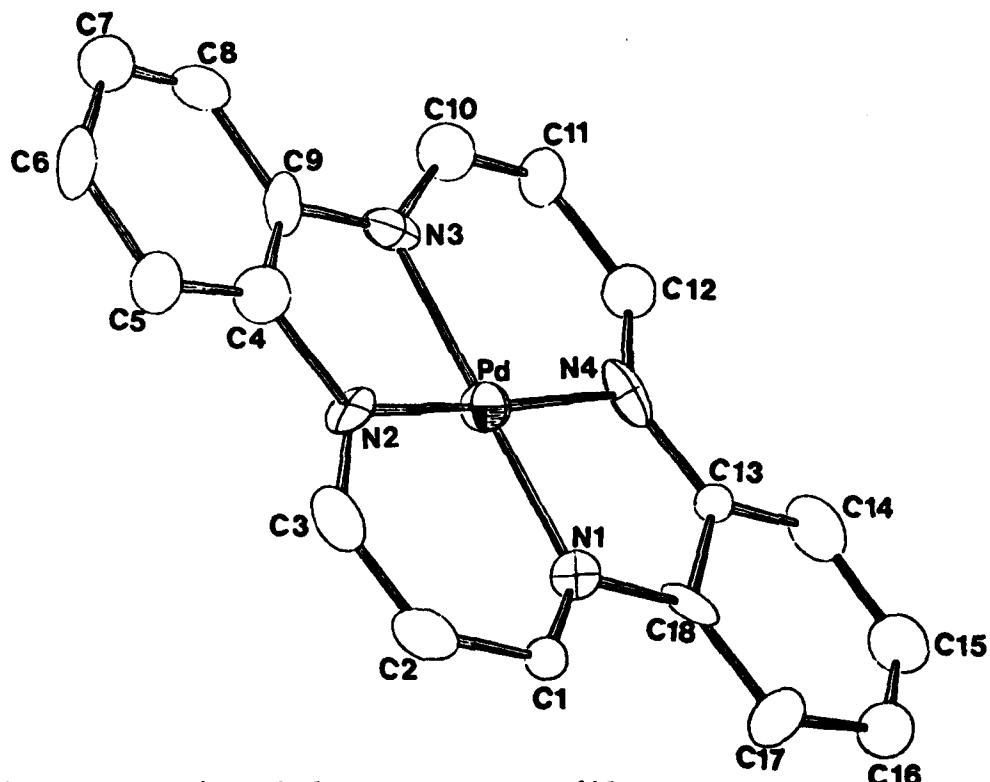


Figure 1. A view of the structure of $\text{Pd}(\text{dB-TAA})$.

The average bond distance in the C4-C9 benzenoid ring is 1.390 Å, and the average angle in the ring is 120.0°. The comparable average bond distance and angle in the C13-C18 ring is 1.397 Å and 120.0°. The internuclear distances between the nitrogen donor atoms in the coordination plane are

N1-N2	2.915(5) Å
N1-N4	2.609(5) Å
N2-N3	2.605(5) Å
N3-N4	2.938(5) Å

In an attempt to find an adequate crystal for a crystallographic study of $\alpha\text{-Pd}(\text{dB-TAA})$, a third crystalline form of $\text{Pd}(\text{dB-TAA})$ was found. This third form, $\gamma\text{-Pd}(\text{dB-TAA})$, crystallizes in the orthorhombic system, space group $\text{Pn}2_1\text{a}$ with the cell dimensions $a = 14.793(3)$, $b = 18.001(6)$, and $c = 5.291(3)$ Å, and $Z = 4$. The gross features of the structure of $\gamma\text{-Pd}(\text{dB-TAA})$ are similar to those of $\beta\text{-Pd}(\text{dB-TAA})$, and the corresponding bond distances and angles are compared with those of $\beta\text{-Pd}(\text{dB-TAA})$ in Table III, where the atom numbering scheme given in Figure 1 is used. The estimated standard deviations for the bond distances and bond angles are somewhat larger than we usually require, but the number of data

Table III. Selected Bond Distances and Angles for β -Pd(dB-TAA) and γ -Pd(dB-TAA)

Bond Lengths, β -Pd(dB-TAA)		Bond Lengths, γ -Pd(dB-TAA)
Pd-N1	1.959(3)	1.925(10)
Pd-N2	1.949(4)	1.935(15)
Pd-N3	1.967(3)	2.011(11)
Pd-N4	1.962(4)	1.984(15)
N1-C1	1.323(5)	1.280(16)
N1-C18	1.422(6)	1.445(14)
C1-C2	1.384(6)	1.498(19)
C2-C3	1.385(6)	1.424(18)
N2-C3	1.328(5)	1.366(21)
N2-C4	1.430(5)	1.437(29)
N3-C9	1.418(6)	1.386(15)
N3-C10	1.318(5)	1.405(19)
C10-C11	1.390(7)	1.250(20)
C11-C12	1.397(7)	1.404(16)
N4-C12	1.309(5)	1.295(22)
N4-C13	1.415(5)	1.376(29)

Bond Angles, β -Pd(dB-TAA)		Bond Angles, γ -Pd(dB-TAA)
N1-Pd-N2	96.41(15)	97.59(.69)
N2-Pd-N3	83.37(15)	81.41(.71)
N3-Pd-N4	96.80(15)	96.66(.79)
N4-Pd-N1	83.41(15)	84.31(.80)
Pd-N1-C1	122.23(32)	127.80(.99)
Pd-N1-C18	113.53(28)	113.12(.78)
Pd-N2-C3	122.99(32)	121.86(1.30)
Pd-N2-C4	113.21(28)	115.30(1.35)
Pd-N3-C9	113.46(28)	112.19(.82)
Pd-N3-C10	121.71(32)	115.84(.98)
Pd-N4-C12	122.80(32)	121.44(1.63)
Pd-N4-C13	113.36(29)	112.68(1.32)
C1-C2-C3	128.21(44)	126.63(1.01)
C10-C11-C12	128.61(43)	126.91(1.34)

were limited and the results are adequate for the purposes of this study.

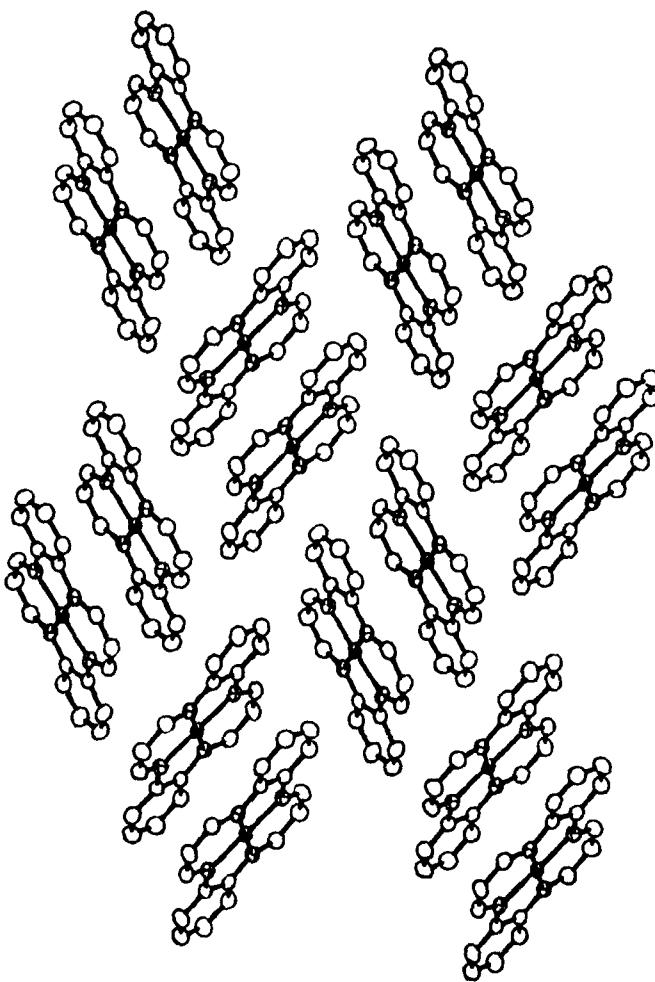


Figure 2. A view of several β -Pd(dB-TAA) molecules projected on the bc plane which shows the formation of cofacial dimers and the packing of the dimers.

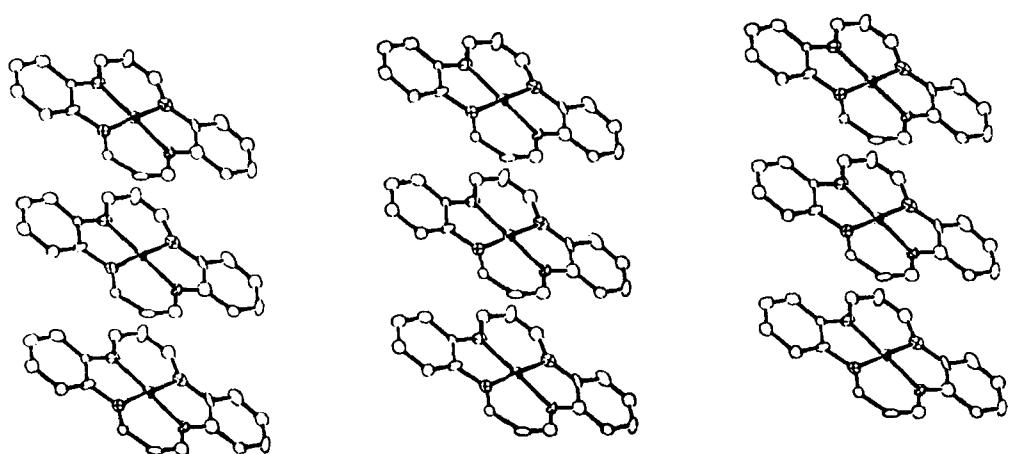


Figure 3. A projection of a segment of the structure of γ -Pd(dB-TAA) on the ac plane which shows the stacking arrangement of the molecular units and the relative orientation of the chains.

As shown in Figure 3, the molecular units in γ -Pd(dB-TAA) stack to form chains which are intimately packed in the solid state. Some close contacts between a given molecule and one related by one translation unit along the Z axis (designated by primes) are

Pd-C ₂ '	3.797(14) Å	N1-N4'	3.899(17)
Pd-C ₃ '	3.541(11) Å	N1-C2'	3.811(12)
Pd-C11'	3.804(16) Å	N1-C12'	3.835(15)
Pd-C12'	3.537(11) Å	N1-C13'	3.756(16)
		N1-Cl4	3.473(15)

The C₂-Pd-C₂' angle is 97.20(.3) $^\circ$. These distances emphasize the slipped nature of the stacking arrangement, which may arise from enhanced van der Waals attractive forces permitted by the stacking pattern. Molecular orbital calculations which are underway on one pair of molecules with the geometry exhibited by δ -Pd(dB-TAA) and a second pair with the geometry in γ -Pd(dB-TAA) are underway and the results may lead to an explanation for the observed packing

arrangements.

DISCUSSION

The observation of three crystalline forms of the precursor compound Pd(dB-TAA) is extremely interesting since all three crystals came from the same batch of material that had been purified by vacuum sublimation. One may conclude that the different crystal forms resulted from crystal growth along the thermal gradient of the cold finger in the sublimation apparatus.

The oxidation of Pd(dB-TAA) with iodine in refluxing chlorobenzene yielded a black solid with stoichiometry $\text{Pd}(\text{dB-TAA})\text{I}_{2.01}$. The resonance Raman exhibited a strong absorption at 105 cm^{-1} with an overtone at 212 cm^{-1} . The 105 cm^{-1} absorption band has been identified as being characteristic of the totally symmetric I-I-I stretching motion.¹² This observation provides evidence for the formulation $\text{Pd}(\text{dB-TAA})(\text{I}_3)_{0.67}$.

The electrical conductivity of the precursor compound $\text{Pd}(\text{dB-TAA})$ is less than $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$. Upon iodination there is a dramatic increase in conductivity with the conductivity of the partially oxidized product being $0.4 \text{ ohm}^{-1} \text{ cm}^{-1}$.

The EPR spectrum of $\text{Pd}(\text{dB-TAA})\text{I}_{2.01}$ shows a broad singlet at $g = 2.004$, and magnetic susceptibility measurements confirms the near diamagnetism expected for the band-like electronic structure. As expected the bands in the infrared spectrum of the partially oxidized material are obscured.

The electronic spectrum of $\text{Pd}(\text{dB-TAA})$ in CHCl_3 differs from that of a Nujol mull of a sample of the material in that the lowest energy band (at 506 nm) is not present in the solution spectrum. This band is likely a result of the stacking arrangement in the solid state. There is an absorption band at 410 nm in $\text{Pd}(\text{dB-TAA})$ which is unaffected by iodination. This band is tentatively assigned to a metal-ligand charge transfer transition, but the assignment can be made more definite once the molecular orbital calculations are completed. An absorption due to the polyiodide could not be made with certainty.

Depending on the length of the reaction time, oxidation of $\text{Pt}(\text{dB-TAA})$ with iodine in near boiling 1,2,3-trichlorobenzene resulted in two complexes with different iodine contents. After 18 hours a material with the composition $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ was obtained, while extending the reaction time to 24 hours afforded a material with a higher iodine content, that being $\text{Pt}(\text{dB-TAA})\text{I}_{1.5}$. Since the resonance Raman of this latter material shows absorption bands

at 114 cm^{-1} and 174 cm^{-1} , it is most reasonable to conclude that the polyiodide is a highly distorted I_3^- or I_5^- moiety.¹²

Iodination of Pt(dB-TAA) leads to a great increase in the electrical conductivity. Of the two samples, the one with the lower iodine content exhibited the higher conductivity at room temperature. The electrical conductivity of $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ is $0.12 \text{ ohm}^{-1} \text{ cm}^{-1}$ (pressed pellet) while that of $\text{Pt}(\text{dB-TAA})\text{I}_{1.5}$ is $0.03 \text{ ohm}^{-1} \text{ cm}^{-1}$.

The room temperature EPR spectra of the iodinated platinum samples consisted of one broad band, respectively, at $g = 2.003$, and magnetic susceptibility measurements on $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ demonstrated that the material was nearly diamagnetic, as expected.

As in the case of Pd(dB-TAA), the low energy transition at 560 nm in the Nujol mull spectrum of Pt(dB-TAA) is the characteristic feature of the stacked structure in the solid state. This transition is either shifted to 625 nm upon iodination, or a new band appears in the Nujol spectrum. A strong absorption band at about 410 nm is unaffected by iodination. The spectrum of $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ is similar to that of $\text{Pt}(\text{dB-TAA})\text{I}_{1.5}$, with the exception that a strong band appears in the spectrum of $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ at about 720 nm. This latter band may be due to the polyiodide, but the resonance Raman spectrum of $\text{Pt}(\text{dB-TAA})\text{I}_{1.35}$ is unavailable at this present time, and a conclusion must await the completion of the experimental work.

CONCLUDING REMARKS

Since it is well known that electrical conductivities of pressed pellets are considerably smaller than the intrinsic conductivities of the materials because of contributions to the resistivity from interparticle contact resistances and because of the inherent anisotropy of low-dimensional systems, there is considerable stimulation for continued efforts to obtain single crystal samples $M(\text{dB-TAA})\text{I}_x$. It is likely that such single crystals will exhibit metal-like conductivities i.e. $d\sigma/dT < 0$, since the conductivities and activation energies of pressed pellet samples of these materials are comparable to those observed for Ni (phthalocyanine)(I_3)_{0.3}, a substance known to exhibit metal-like conductivity.^{5b}

The relatively long palladium-palladium distances in the stacked and dimeric forms of Pd(dB-TAA) leads to the conclusion that metal-metal interactions do not contribute significantly to any band formation, and that intermolecular interactions occur between the π -orbitals of partially oxidized macrocyclic complexes.

ACKNOWLEDGEMENT

This research was supported in part by the Office of Naval Research. I am grateful to my colleagues for their continued interest and collaboration in this research.

REFERENCES

1. Current research activities are summarized in the following proceedings:
 - a. Baristic, S.; Bjelis, A.; Cooper, J.R.; Leontic, B. "Quasi-One-Dimensional Conductors"; Notes in Physics; Springer-Verlag: Berlin, 1979; Vol. 95, 96.
 - b. Hatfield, W.E. "Molecular Metals"; NATO Conference Series VI; Plenum: New York, 1979; Vol. 1.
 - c. Miller, J.S.; Epstein, A.J. "Synthesis and Properties of Low-Dimensional Materials"; Anal of the New York Academy of Sciences; New York Academy of Sciences, 1978; Vol. 313.
2. Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. J. Phys. Letters 1980, Feb. 15.
3. Weiss, M.C.; Gordon, G.; Goedken, V.L. Inorg. Chem. 1977, 16, 305.
4. M. Tsutsui and R. Boxsein prepared samples of a number of these compounds and the UNC Group carried out physical measurements. This joint research will be described in detail elsewhere.
5. a. Peterson, J.L.; Schramm, C.J.; Stojakovic, D.R.; Hoffman, B.M.; Marks, T.J. J. Am. Chem. Soc. 1977, 99, 286.
b. Schramm, C.J.; Stojakovic, D.R.; Hoffman, B.M. Marks, T.J. Science 1978, 200, 47.
c. Wright, S.K.; Schramm, C.J.; Phillips, T.E.; Scholler, D.M.; Hoffman, B.M. Synthetic Metals 1979/80, 1, 43.
6. Corvan, P.J.; Lau, C.P.; Hatfield, W.E. manuscript in preparation.
7. Brown, D.B.; Crawford, V.H.; Hall, J.W.; Hatfield, W.E.; J. Phys. Chem. 1977, 81, 1303.
8. Figgis, B.N.; Lewis, J.; In "Modern Coordination Chemistry", Lewis, J. And Wilkins, R.C., Editors, Interscience Publishers, Inc.: New York, 1960; Chapter, 6; Page 403.
9. König, E., "Magnetic Properties of Transition Metal Compounds", Springer-Verlag: Berlin; 1966.

10. Weller, R.R.; Hatfield, W.E.; J. Chem. Ed. 1979, 56, 652.
11. Hatfield, W.E.; Hodgson, D.J.; Brookhart, M.; Corvan, P.J.; Lau, C.F.; Marsh, W.E.; Boxsein, R.; Tsutsui, M. manuscript submitted for publication.
12. Cowie, M.; Gleizes, A.; Gryniewich, G.W.; Kalina, D.W.; McClure, M.S.; Scaringe, R.P.; Teitelbaum, R.C.; Ruby, S.L.; Ibers, J.A.; Kannewurf, C.R.; Marks, T.J. J. Am. Chem. Soc. 1980, 101, 2921, and references therein.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u>	<u>Copies</u>
------------	---------------

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

A. M. Anzalone
ARRADCOM
Plastics Technical Evaluation Center
Bldg. 3401
Dover, New Jersey 07801

TECHNICAL REPORT DISTRIBUTION LIST, 053

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. R. N. Grimes Department of Chemistry University of "irginia Charlottesville, Virginia 22901	1	Professor H. Abrahamson Department of Chemistry University of Oklahoma Norman, Oklahoma 73019	1
Dr. M. F. Hawthorne Department of Chemistry University of California Los Angeles, California 90024	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. D. B. Brown Department of Chemistry University of Vermont Burlington, Vermont 05401	1	Dr. B. Foxman Department of Chemistry Brandeis University Waltham, Massachusetts 02154	1
Dr. W. B. Fox Chemistry Division Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. J. Adcock Department of Chemistry University of Tennessee Knoxville, Tennessee 37916	1	Dr. G. Geoffrey Department of Chemistry Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. A. Cowley Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. J. Zuckerman Department of Chemistry University of Oklahoma Norman, Oklahoma 73019	1
Dr. W. Hatfield Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1	Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. D. Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Professor Ralph Rudolph Department of Chemistry University of Michigan Ann Arbor, Michigan 48109	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1
		Professor R. Neilson Department of Chemistry Texas Christian University Fort Worth, Texas 76129	1

TECHNICAL REPORT DISTRIBUTION LIST, 053

No.
Copies

Professor M. Newcomb
Texas A&M University
Department of Chemistry
College Station, Texas 77843 1

Professor Richard Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627 1